U.S. DEPARTMENT OF COMMERCE PATENT & TRADEMARK OFFICE

B/O Form PTO-1390 **Transmittal Letter to the United States Designated/Elected Office (DO/EO/US) Concerning a Filing Under *35 USC 371***		*Attorney's Docket Number* REF/EDWARDS/047
		U.S. Application Number (if known) 09/508512
International Application Number PCT/EP98/06047	*International Filing Date* 22 September 1998	*Priority Date Claimed* 24 September 1997
Title of Invention SELECTIVE MONITORING OF TRITIUM-CONTAINING SPECIES IN A GAS		
Applicant(s) for DO/EO/US EDWARDS et al.		

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items under *35 USC 371*:

1. ☒ This is a **FIRST** submission of items concerning a filing under *35 USC 371*.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under *35 USC 371*.
3. ☒ This express request to begin national examination procedures *(35 USC 371(f))* at any time rather than delay examination until the expiration of the applicable time limit set in *35 USC 371(b)* and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed *35 USC 371(c)(2)*.
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English *(35 USC 371(c)(2))*.
7. ☒ Amendments to the claims of the International Application under PCT Article 19 *(35 USC 371(c)(3))*
   a. ☒ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 *(35 USC 371(c)(3))*.
9. ☒ An oath or declaration of the inventor(s) *(35 USC 371(c)(4))*. (☒ Executed ☐ Unexecuted)
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 *(35 USC 371(c)(5))*.

Items 11 to 16 below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under *37 CFR 1.97* and *1.98*.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with *37 CFR 3.28* and *3.31* is included.
13. ☒ A **FIRST** preliminary amendment.
    ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: Verified Small Entity Statement by Nonprofit Organization

Application Number (if Known) 09/508512	International Application Number PCT/EP98/06047	Attorney's Docket Number REF/EDWARDS/047	
		Calculations	**PTO USE ONLY**

17. The following fees are submitted:

Basic National Fee *(37 CFR 1.492(a)(1)-(5))*:

- ☒ Search report has been prepared by the EPO or JPO $840.00
- ☐ International Preliminary Examination Fee paid to USPTO *(37 CFR 1.482)* $670.00
- ☐ No International Preliminary Examination Fee paid to USPTO *(37 CFR 1.482)* but International Search Fee paid to USPTO *(37 CFR 1.445(a)(2))* $760.00
- ☐ Neither International Preliminary Examination Fee *(37 CFR 1.482)* nor International Search Fee *(37 CFR 1.445(a)(2))* paid to USPTO $970.00
- ☐ International Preliminary Examination Fee paid to USPTO *(37 CFR 1.482)* and all claims satisfied provisions of PCT Article 33(1)-(4) $96.00

					$840.00
ENTER APPROPRIATE BASIC FEE AMOUNT				**$**	**840.00**
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date *(37 CFR 1.492(e))*.					
CLAIMS	**NUMBER FILED**		**NUMBER EXTRA**	**RATE**	
Total Claims	39	-20 =	19	× $18.00	$ 342.00
Independent Claims	2	-3 =	0	× $78.00	$ 0.00
Multiple Dependent Claims (if applicable)				+ $260.00	
TOTAL OF ABOVE CALCULATIONS				**$**	//8 ~~2342.00~~
Reduction by ½ for filing by small entity, if applicable. Verified Small Entity Statements must also be filed (Note *37 CFR 1.9, 1.27, 1.28)*				$	591.00
SUBTOTAL				**$**	**591.00**
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date *(37 CFR 1.492(f))*.					
TOTAL NATIONAL FEE					
Fee for recording the enclosed assignment *(37 CFR 1.21(h))*. The assignment must be accompanied by an appropriate cover sheet *(37 CFR 3.28, 3.31)*. **$40.00** per property.				$	40.00
TOTAL FEES ENCLOSED				**$**	**631.00**
Amount to be:				Refunded:	
				Charged:	

a. ☒ A check in the amount of $631.00 to cover the fees is enclosed.

b. ☐ Please charge my **Deposit Account Number 02-0200** in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to **Deposit Account Number 02-0200**. A duplicate copy of this sheet is enclosed.

Note: Where an appropriate time limit under *37 CFR 1.494* or *1.495* has not been met, a petition to revive *(37 CFR 1.137(a) or (b))* must be filed and granted to restore the application to pending status.

BACON & THOMAS, PLLC
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ALEXANDRIA, VIRGINIA 223124-1176
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DATE: March 24, 2000

Respectfully submitted,

Richard E. Fichter

Richard E. Fichter
Attorney for Applicant
Registration Number: 26,382

Applicant or Patentee: EURATOM
Serial or Patent Number: PCT/EP98/06047
Filed or Issued: 22.09.98
For:

Docket #:
Examiner:
Art Unit:

VERIFIED STATEMENT (DECLARATION) BY A NONPROFIT ORGANIZATION CLAIMING SMALL ENTITY STATUS UNDER *37 CFR 1.9(F) AND 1.27(D)*

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

Name of Organization: EUROPEAN ATOMIC ENERGY COMMUNITY

Address:

Type of Organization

- ☐ University or other institution of higher education.
- ☐ Tax exempt under Internal Revenue Service code *(26 USC 501(a) and 501(c)(3))*.
- ☐ Nonprofit scientific or educational under statute of state of the United States of America.
  Name of State: ______ Statute: ______
- ☐ Would qualify as tax exempt under Internal Revenue Service code *(26 USC 501(a) and 501(c)(3))* if located in the United States of America.
- ☐ Would qualify as nonprofit scientific or educational under statute of state of the United States of America if located in the United States of America.
  Name of State: ______ Statute: ______

I hereby declare that the nonprofit organization identified above qualifies as a nonprofit organization as defined in *37 CFR 1.9(e)* for purposes of paying reduced fees under *section 41(a) or (b) of Title 35, United States Code* with regard to the invention entitled SELECTIVE MONITORING OF TRITIUM CONTAINING SPECIES IN A GAS

by P. Pacenti, R. Edwards
(Inventor(s))

described in:

- ☐ The specification filed herewith.
- ☐ Application serial number ______, filed ______.
- ☐ PCT International patent application number PCT/EP98/06047, filed 22 September 1998.
- ☐ Patent number ______, issued ______.

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the above identified invention.

If the rights held by the above identified nonprofit organization concern are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under *37 CFR 1.9(d)* or by any concern which would not qualify as a small business concern under *37 CFR 1.9(d)* or a nonprofit organization under *37 CFR 1.9(e)*. *Note: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities *(37 CFR 1.27)*.

Full Name:

Address:

☐Individual ☐Small Business Concern ☐Nonprofit Organization

☐See attached sheet for additional person(s), concern(s) or organization(s).

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate *(37 CFR 1.28(b))*.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine, or imprisonment, or both, under *section 1001 of Title 18 of the United States Code*, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which the verified statement is directed.

Giulio Cesare GRATA
Name

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L-2920 Luxembourg
City, State, Zip, Country

J. N. DURVY
Signature

06. 03. 2000
Date

en l'absence de
G. Grata

European Atomic Energy Community – The Commission – EURATOM

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

EDWARDS et al.

U.S. National Phase of PCT/EP98/06047

Entry papers filed herewith March 24, 2000

Attention: PCT OFFICE

For: SELECTIVE MONITORING OF TRITIUM-CONTAINING SPECIES IN A GAS

PRELIMINARY AMENDMENT
AND INFORMATION DISCLOSURE STATEMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

The present application is the U.S. national phase of international application number PCT/EP98/06047. The following amendments pertain to the claims as amended.

Please note that the amended pages 18-24 attached to the International Preliminary Examination Report (Annexes) and submitted herewith, have replaced the originally filed pages 18-24 of the application. The claims to be examined and amended by this preliminary amendment are found on amended pages 18-24.

Please amend the above-identified application as follows:

IN THE SPECIFICATION:

Please add the attached ABSTRACT OF THE DISCLOSURE to the application.

IN THE CLAIMS:

Claim 3, line 2, please cancel "or 2".

Claim 5, lines 1 and 2, please cancel "any preceding claim" and insert - -claim 1- -.

Claim 6, lines 1 and 2, please cancel "any preceding claim" and insert - -claim 1- -.

Claim 7, lines 1 and 2, please cancel "any preceding claim" and insert - -claim 1- -.

Claim 8, lines 1 and 2, please cancel "any preceding claim" and insert - -claim 1- -.

Claim 11, line 5, please cancel "any of claims 1 to 7" and insert - -claim 1- -.

Claim 15, lines 1 and 2, please cancel "any one of claims 9 to 14" and insert - -claim 9- -.

Claim 16, line 1, please cancel "any of claims 11 to 15" and insert - -claim 11- -.

Claim 17, lines 1 and 2, please cancel "any one of claims 9 to 16" and insert - -claim 9- -.

Claim 19, line 1, please cancel "or 18".

Claim 20, line 1, please cancel "any of claims 11 to 19" and insert - -claim 11- -.

Claim 21, lines 3 and 4, please cancel "according to any of claims 1 to 7,".

Claim 22, line 1, please cancel "any of claims 9 to 21" and insert - -claim 9- -.

Claim 23, line 5, please cancel "any of claims 1 to 7" and insert - -claim 1- -.

Claim 25, line 1, please cancel "or 24".

Claim 26, lines 1 and 2, please cancel "any of claims 23 to 25" and insert - -claim 23- -.

Claim 27, line 1, please cancel "or 26".

Claim 28, lines 1 and 2, please cancel "any of claims 23 to 27" and insert - -claim 23- -.

Claim 29, lines 1 and 2, please cancel "any of claims 23 to 28" and insert - -claim 23- -.

Claim 30, lines 1 and 2, please cancel "any of claims 23 to 29" and insert - -claim 23- -.

Claim 33, line 1, please cancel "claims 31 or 32" and insert - -claim 31- -.

Claim 34, lines 1 and 2, please cancel "any of claims 23 to 33" and insert - -claim 23- -.

Claim 35, lines 3 and 4, please cancel "according to any of claims 1 to 7,".

Claim 36, lines 1 and 2, please cancel "any of claims 23 to 35" and insert - -claim 23- -.

Claim 37, line 2, please cancel "according to any of claims 1 to 5".

REMARKS

Applicants have amended the claims in order to reduce the initial filing fee by deleting the multiple dependent claims from the application. Applicants retain the right to reintroduce any subject matter canceled by the present Amendment at any time during the prosecution of this application or any further application claiming benefit of this application.

Applicants have amended the application to substitute the originally filed pages 18-24 with the amended pages 18-24 attached to the International Preliminary Examiner Report (Annexes) and included in the application as filed herewith. Also, an Abstract of the Disclosure has been added to the application.

Applicants are submitting herewith a copy of the Search Report which issued on International Application No. PCT/EP98/06047, of which the present application is the U.S. national phase. All of the publications cited in the International Search Report are listed on the attached Form PTO-1449. It is Applicants' understanding that, under the procedures of the PCT, copies of the cited publications will have been supplied to the U.S. Patent Office by the International Bureau. However, the Examiner is invited to contact the undersigned attorney if additional copies are necessary or would facilitate examination of the present application.

Otherwise, the Examiner is respectfully requested to return an initialed and dated copy of the attached Form PTO-1449 to confirm that all publications listed thereon have been considered and made officially of record in the file of this application.

Applicants understand that, under the procedures of the PCT, a copy of the priority document (9720371.5, filed 24 September 1997) will have been supplied to the

U.S. Patent Office pursuant to Rule 17 of the PCT Regulations. It is therefore respectfully requested that the first Official Action in the present application contain an indication that the appropriate priority document is in the file of this application.

In view of the above amendments, an early action on the application is now in order and is most respectfully requested.

Respectfully submitted,
BACON & THOMAS, PLLC

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DATE: March 24, 2000

SELECTIVE MONITORING OF TRITIUM-CONTAINING SPECIES IN A GAS

The present invention is concerned with a method and apparatus for selectively monitoring hydrophilic tritium-containing species in a gas, and in particular with such a method and apparatus which selectively monitors hydrophilic tritium-containing species in the air of a controlled area for tritium handling.

Tritium is an isotope of hydrogen which undergoes radioactive decay by emission of a beta-particle. The most common forms of tritium encountered in air are the elemental forms HT, DT or T2 (usually referred to generically as HT) and the oxidised forms HTO, DTO and T2O (usually referred to generically as HTO). The elemental form of tritium has a radiotoxicity 25000 times lower than the oxidised form, according to the International Commission on Radiation Protection. This is because, whereas the oxidized form mixes thoroughly with water in the lungs, the elemental form is hardly absorbed at all and shows a slow rate of isotope exchange with water in the body. It is also thought that the absorption of HT has been somewhat underestimated, so that a HTO/HT radiotoxicity ratio of as low as 1000 may be more appropriate.

Other tritiated molecules, such as tritiated hydrocarbons, methanol etc., can often be present in the gas. The radiotoxicities of these species depends on the extent to which they enter, or exchange tritium with, water in the lungs.

Clearly it is important to distinguish between the chemical forms of tritium, especially between the most common forms; oxidized and elemental; because of the large difference in radiotoxicity.

Presently tritium is monitored either without discriminating between the aforementioned two main chemical forms, by, for example, using ionisation chambers, internal gas-proportional counters or the like, or using scintillators of various kinds, such as, for example, anthracene, or the like. Other means include delayed methods that separate the humidity from the air, for example, by absorption in a bubbler, desiccation, condensation or freezing. The sample must then be measured by, for example, liquid scintillation counting or alternatively by one of the above identified methods.

Monitoring and measurement of tritium concentration in ambient air, is generally carried out using monitors such as ionisation chambers.

One type of monitor, selective for tritiated water, which has been previously used is generally based on two ionisation chambers connected by a selectively permeable (Nafion-Dupont) membrane. Such a monitor has been developed so as to discriminate between HTO and HT concentrations in a gas. Monitors of this type generally suffer from the disadvantage that they have a limited discrimination factor due to the permeability of the membrane for both HTO and HT. Furthermore, they can take long periods of time to perform the necessary measurements due to the time-period which is sufficient for the gas to penetrate the membrane. Such systems are also typically bulky and expensive.

Another type of HTO-selective monitor consists of two ionization chambers in series, separated by a drier. The HTO concentration is deduced by subtracting the signal emitted by the second ionization chamber from that of the first ionization chamber. A disadvantage

of this type of system is that, if HT is present in higher concentrations than HTO, the errors in the ionization chamber measurements may greatly exceed the HTO concentration. The system is also bulky and expensive.

It is an object of the present invention to alleviate such disadvantages, and additionally to provide a novel method and apparatus which can discriminate between the oxidised and elemental forms of tritium in a gas.

Therefore, according to a first aspect of the present invention there is provided a hygroscopic scintillator, suitable for selective response to tritiated water vapour and other hydrophilic tritiated species in a gas, which scintillator comprises a solid scintillator material having a layer of hygroscopic material thereon. Such a scintillator advantageously allows tritiated water vapour or other hydrophilic gas species, such as, for example, tritiated ammonia, tritiated methanol or the like to enter or exchange tritium, holding the tritium from said species in close proximity to the surface of the solid scintillator material.

The range of beta-emission from tritium (average about 0.4 microns in liquid water) allows the tritium in the hygroscopic layer to excite the solid scintillator component of the hygroscopic scintillator element. Advantageously, the hygroscopic material may comprise a layer of any hygroscopic or deliquescent substance such as a solution of deliquescent compound, or an aqueous gel of said compound. In one embodiment a hydrated solid or zeolite may be used which has the advantage that for some desired applications they are selective only for tritiated water, and not other

hydrophilic species.

The range of tritium beta-emissions being limited, only the surface region of the scintillator material of the scintillator element contributes to the monitor sensitivity. Therefore said scintillator material may advantageously be provided in a form which comprises a high specific surface area, for example as a sheet, as fibres, powder, powder compact, paint, varnish or a combination of the said forms.

There is provided by a second aspect of the present invention a method of monitoring tritiated water vapour or other tritiated species activity in a gas, which method comprises contacting said gas with a scintillator according to the invention, said scintillator being enclosed in a substantially light tight container, and measuring the light emitted from said hygroscopic scintillator, the amount of said emitted light providing a measure of the tritiated activity of said gas.

The method according to this aspect of the present invention advantageously discriminates between the oxidised form of tritium in a gas, and the elemental form of tritium, the oxidised form of tritium being highly radio-toxic compared to the elemental form.

Furthermore, during operation the hygroscopic scintillator element contains an amount of HTO typically contained in a volume of gas much larger than the volume of the element. Therefore, the method according to the first aspect of the present invention advantageously allows a much more compact format than an ionization chamber sensitive to the same activity of HTO in gas.

Advantageously, the method according to this aspect of the present invention may have a sensitivity to all tritium-containing species in the gas, substantially in proportion to the amount in which they enter or exchange tritium with the water-containing layer in the hygroscopic scintillating element. Since the relative radiotoxicity of the tritiated species depends substantially on their entry and isotope-exchange with water in the human lung, the method provides a good indication of the overall radiotoxicity of the gas mixture due to all tritium species present.

Solid scintillators advantageously emit light when subjected to beta-emissions from tritium, and, unlike liquid scintillation cocktails, have a stable geometrical form and negligible evaporation rates. Preferably, the scintillator according to the invention may be, for example, a plastic, a glass, an inorganic "phosphor" (e.g. doped zinc sulphide), an oxide-based material (e.g. Yttrium Aluminium Garnet "YAG" or Yttrium Aluminium Perovskite "YAP": crystalline oxides available in transparent single crystal form), or a combination of these materials, none of which absorb significant quantities of water.

Advantageously, to improve wetting, the solid scintillator material may be pre-treated on the surface with a detergent, or subjected to a hydrophilic surface treatment such as sulfonation or the like; or alternatively detergent may added to the aqueous component.

Preferably, a light guide may be provided to help transmit light from the scintillator to the light detector(s). In some cases, the solid scintillator material itself may act as a light guide. Preferably,

where the detectors are, for example, remote from said scintillator element and outside any light tight container, the light guide may be of a material which prevents entry or exit of any light.

When measuring tritiated activity in a process gas, such as, air, the humidity of the air can affect the reading in two ways. Firstly, for a given activity of tritiated water, for example, in the gas (in terms of Becquerel per cubic meter of gas), the concentration of tritium per gram of water is inversely proportional to the humidity of the gas. This effect tends to decrease the sensitivity of the monitor (in terms of Becquerel per cubic meter of gas) as the humidity increases. Secondly, the amount of water present in the hydrated layer increases with the humidity, depending on the absorption characteristics of the hygroscopic material. This in turn tends to increase the amount of water contributing to the scintillation, and hence tends to increase the output of the monitor as humidity increases. Therefore, the two effects tend to cancel each other. Preferably, by optimizing the nature and thickness of the layer of hygroscopic material, the variation in sensitivity of the output with changing humidity in the gas can be minimized.

In a preferred embodiment of this aspect of the present invention, the light emitted by the hygroscopic scintillator element is measured by one or more light detectors which include photomultipliers, multichannel plates, or photodiodes or the like which would be well known to those skilled in the art. The electronics associated with such light detectors may use conventional current-pulse-counting, each pulse corresponding substantially to a light pulse from a scintillation event. As is usual for scintillation techniques, the rate of current pulses is

substantially proportional to the rate of scintillation events. Where two or more light detectors are used, one may advantageously reduce noise background by well-known pulse coincidence detection techniques. If the light output is sufficient, continuous average-current monitoring may be used instead of pulse counting.

In one embodiment of this aspect of the present invention the gas to be monitored may be air. Thus, advantageously, the method may be used to monitor tritium intake, for example, by radiation workers in a controlled handling area. In a preferred embodiment the air tritium monitor may be small enough to be portable which may therefore allow it to be carried continuously by workers in a controlled area.

In another embodiment of this aspect of the present invention, the gas to be monitored may be enclosed in a chemical plant: an application normally described as a "process monitor". In a light-tight plant, the monitor may be inserted through the plant wall (for example into a pipe or storage tank) without the need for its own light-tight container.

Preferably, such a process monitor may be used in conjunction with a non-discriminating monitor in order to measure, by difference, the concentrations in gas or air of both tritiated water (possibly together with hydrophilic species) and elemental tritium (possibly together with other hydrophobic species). In this embodiment, the non-discriminating tritium monitor may be substantially identical to the discriminating monitor comprising a scintillator element according to the invention with the exception that the hygroscopic layer is omitted in the non-discriminating monitor.

Preferably, a second radiation monitor; preferably substantially identical to the said discriminating monitor, but sealed in a container free of radioactive gas, may be provided to compensate for background radiation fields (e.g. gamma-radiation), by subtraction: an analogous technique is already used for compensating ionization chambers for radiation background.

According to a further aspect of the invention there is provided apparatus for monitoring the level of tritiated water and other tritiated hydrophilic species in a gas, which apparatus comprises, a hygroscopic scintillator according to the invention, and means for measuring the amount of light emitted from said hygroscopic scintillator element. In one embodiment of this aspect of the invention, means may be provided for contacting said gas with said hygroscopic scintillator. The measuring means may either be connected to said hygroscopic scintillator element or may be provided remotely from it by means of a light guide.

Thus, advantageously, the apparatus according to this aspect of the invention allows for a measure of the level of tritium in a gas, such as air, to be provided. The apparatus responds with much greater sensitivity to tritiated species, such as tritiated water vapour, which are more radiotoxic because they mix or exchange hydrogen isotopes rapidly with water.

This further aspect of the present invention may be provided in the form of a stand-alone room air monitor, a personal tritium monitor or an "in-line" process gas monitor for mounting with tube connectors in the pipework of a chemical process using tritiated gas.

In one embodiment of this aspect of the invention the hygroscopic scintillator may be enclosed in a substantially light-tight container with a window(s) or aperture(s) being provided therein to allow emitted light to reach the light detector(s), in addition to an inlet adapted to allow access of said gas to the hygroscopic scintillator element but to prevent light escaping from or entering said container. An outlet may also be provided to allow flow of said gas over or through the hygroscopic scintillator element from said inlet to said outlet. Preferably, said inlet and outlet minimize the entry of external light by, for example, the use of dark or black materials and which may have a geometry which forces the light to make multiple reflections before reaching the monitor.

For a stand-alone room air monitor, a pump may preferably be provided to pass air continuously through the monitor. Furthermore, a dust filter may be mounted at the inlet. When the apparatus is used as a personal tritium monitor, a pump may be provided, or alternatively the monitor may be built into a breathing mask so that the flow of air is provided by the breathing of the worker. Furthermore, when used as a process gas monitor, a pump may be used to pass gas therethrough if the gas flow or pressure drop available inside the plant is insufficient. Such an application could be, for example, the monitoring of tritium in an inert-gas glovebox. The pump may be of many types, for example, including a membrane pump, an electrical fan or impeller, a centrifugal pump or advantageously (for reason of low power consumption) a piezo-electric fan built into a housing. Thus advantageously the apparatus according to the invention may provide a substantially continuous and accurate monitoring of the tritium radiotoxicity in a gas.

The apparatus in an alternative embodiment may also be provided in the form of a "nude" monitor for process gas in an existing light-tight tank or pipe. Lacking its own light-tight casing, the apparatus according to the invention may be fixed to an aperture in the plant wall or pipe with a substantially light-tight seal. In this embodiment, gas flow through or over the hygroscopic scintillator element may be provided by the existing flows inside the plant, or alternatively by a fan.

Advantageously, the apparatus according to the present invention uses a hygroscopic material coated onto a solid scintillator to make a hygroscopic scintillating element. Said hygroscopic layer may consist of a layer of a hygroscopic or deliquescent substance such as a solution of deliquescent compound, or an aqueous gel of said compound. Many compounds are suitable examples included but are not limited to zinc chloride, potassium acetate, phosphoric acid, lithium chloride. Alternative types of hygroscopic layers could consist of a hygroscopic organic solid or liquid, for example, poly-(ethylene oxide), a soap, sugar, polyhydroxymethylemethacrylate or a glycol. The use of a gel containing deliquescent compound may advantageously impede long-term redistribution of the hygroscopic layer across the surface. A hydrated solid such as, for example, zeolite may also be used in said hygroscopic layer. Although having a relatively slow exchange rate of water with the water vapour in the gas, this embodiment has the advantage in some special applications of being selective only for tritiated water, and not other hydrophilic species.

The solid scintillator material, or a combination of solid scintillator materials, may advantageously be

applied as a paint (e.g. zinc sulphide paint) or varnish (e.g. plastic scintillator dissolved in organic solvent, possibly mixed with YAP powder) to the surface of the light guide. The advantages are a reduction in cost of scintillator material, efficient light collection, and relative insensitivity to gamma radiation, due to the small mass of solid scintillator present. In other foreseen designs the solid scintillator may function as a light guide.

In the apparatus according to the invention, the inner walls of the light-tight container, or the surface of a light guide, may preferably be made reflective, for example by polishing or aluminizing, to improve light collection efficiency.

The apparatus according to the invention has a certain sensitivity to HT and other hydrophobic tritiated species due to the arrival at the scintillator of tritium beta emissions arising from such species in the gas in and around the scintillator element, the range of tritium emissions in gas being much greater than in condensed phases. This sensitivity to HT is approximately proportional to the volume of gas in and around the scintillator element. It is possible to vary the relative sensitivity to HT, for a given HTO sensitivity, by keeping the same surface area and preparation method for the hygroscopic scintillator element, but varying its overall size to change the gas space inside the scintillating element. Alternatively, extra scintillator material may be added which is not covered by a hygroscopic layer. Thus the ratio of HTO to HT sensitivity may be adjusted to match a desired value, for example 1000.

Preferably, the measuring means for measuring light emitted by the hygroscopic scintillator element

comprises one or more light detectors, including photomultipliers, multichannel plates with photodiode detectors, or photodiodes. The electronics associated with such light detectors may use conventional current-pulse-counting, each pulse substantially corresponding to light pulse from a scintillation event. As usual for scintillation techniques, the rate of current pulses is substantially proportional to the rate of scintillation events. Where two or more light detectors are used, one may advantageously reduce noise background by well-known pulse coincidence detection techniques. If the light output is sufficient, continuous average-current monitoring may be used instead of pulse counting.

Preferably, electronics are provided to convert the rate of charge pulses or average current into a signal which is substantially proportional to the radiotoxicity of the gas, or its logarithm. Said signal may preferably be displayed on a meter or digital display and/or converted to an audible signal, and/or made available as an output to a computer, data-logger or other external recording or control apparatus. A standard humidity gauge may be incorporated into the monitor, or a separate humidity gauge may be read into said recording and control apparatus, in order to allow automated or manual compensation for the effects of gas or air humidity on the sensitivity of the present tritium monitor or apparatus according to the invention. Furthermore, it is foreseen that the function of said humidity gauge may be incorporated into the monitor by measuring the electrical AC or DC conductivity of the hygroscopic layer, for example by measuring the resistance between two metallic contacts applied to the surface of the solid scintillator before coating with the hygroscopic layer.

The invention may be more clearly understood by the following description of an embodiment thereof, with reference to the accompanying drawing given by way of example only, wherein

Figure 1 is an illustration of apparatus for monitoring the tritiated water content, or more generally, radiotoxicity of a gas containing tritium species, according to the invention.

Figures 2 to 6 illustrate alternative embodiments of the apparatus of Figure 1. In each figure there is shown one or more light detectors, and a hygroscopic scintillator element. Some designs have a light guide incorporated therein.

Referring to the drawings and initially to Figure 1, there is shown a simple design for a hygroscopic scintillator element according to the invention incorporated into a monitor 1. In use the monitor functions when gas 2 passes over one surface of a flat hygroscopic scintillator element 3, which can be supported by a backing plate 14. In this embodiment no light guide is provided and the scintillation light pulses emitted from the element 3 pass through the sample gas 2 to reach the light detector 4. This design is particularly suitable for fragile scintillator elements: powder compacts and the like and for layers of substantially opaque and non-porous solid scintillator, such as paints of inorganic phosphors (e.g. doped zinc sulphide paint).

The monitor 5 illustrated in Fig.2 is of similar geometry to the monitor of fig. 1 except that the gas 6 passes through a porous hygroscopic scintillator element 7, for example a porous powder compact supported on a filter 8. In this case, the amount of

hygroscopic material applied to the powder compact should be limited, not to block the passage of the test gas. The light pulses emitted from the scintillator element 7 reach the light detector 9.

The monitor 10 illustrated in Figure 3 comprises a simple geometry with high light collection efficiency which is achieved by coating a thin layer of solid scintillator material 11 onto the face of a light guide 12, before applying the hygroscopic layer. Even more simply, it is possible to eliminate the light guide 12, applying the solid scintillator directly onto the face of the light detector 13.

Fig.4 illustrates a monitor 20 comprising parallel sheets of solid scintillator (e.g. plastic, glass, scintillating crystal) 21, having the hygroscopic layer coated thereon, and glued (using transparent glue) inside a channel 22 traversing a light guide 23. The same overall geometry may be realized by making the sheets from the light-guide material, and then coating them with a layer of solid scintillator, before applying the hygroscopic layer.

The overall geometry shown in fig.4 can alternatively be obtained by making it from a single block of plastic or resin: e.g. by injection moulding which can act as a light guide. The surfaces of the parallel plates are then coated first with a solid scintillator and then with a hygroscopic layer.

In monitor 30 illustrated in figure 5, solid scintillator fibres 31 are coated with the hygroscopic layer and held in a tube 32: the fibres themselves acting as light guides. The same geometry can be obtained by first coating non-scintillating transparent fibres with a layer of solid scintillator.

Figure 6 illustrates a monitor 40 a single light-detector 44 with a spiral of hygroscopically-coated plastic scintillator sheet 41 glued onto the end-plate of the light guide 42, which forces the gas to spiral inwards towards the central outlet tube (reverse flow is also possible). Fig.7 shows a similar hygroscopically coated scintillator element, this time with axial gas flow and no light guide.

Figures 4,5 and 7 show double light detectors, to enable background noise reduction by coincidence detection. In each case, one of the two detectors can be replaced by a reflector if pulse coincidence detection is not desired. Conversely, in the other designs, two light detectors may be used instead of one to allow pulse coincidence detection: they can both view the same side of the hygroscopic scintillator element where it is not advantageous to mount the detectors on opposite sides (e.g. if the scintillator is opaque).

Prototype monitors and initial results

To be of use, the monitor must have a limit-of-detection for HTO below the limit set by the International Commission on Radiation Protection for the HTO concentration in air which may be breathed by workers. This value is the derived air concentration (DAC), and equals 8×10^5 Bq/m3.

Two monitors were constructed using hygroscopically-coated plastic scintillator in sheet form. The geometries of the monitors corresponded to those illustrated in fig.4 and fig. 6. After forming the scintillator sheet into a spiral (fig. 6) or gluing the sheets in position (fig.4), the surface of the plastic scintillator material was treated with non-ionic detergent, dried in air, painted with a layer of

zinc chloride solution, and the excess blown off with compressed air. By varying the concentration of the zinc chloride (a strongly deliquescent salt) it was possible to produce a continuous solution layer about 1 micron thick, in equilibrium with the humidity of room air. This was found to be about the optimum thickness for giving a combination of good sensitivity and fast response to changing HTO concentrations in the passing gas.

Subsequently, a third prototype monitor was made using the geometry illustrated in fig 2. In this case the scintillator element 7 was made using a compacted layer of YAP powder mounted on a glass-fibre filter. This was wetted with detergent, dried and then a certain amount of zinc chloride solution was uniformly applied to render it hygroscopic; in the first tests 2mg of solution was applied (weighed when in equilibrium with ambient air at 58% relative humidity).

Air loaded with 30% relative humidity of either plain water vapour or tritiated water vapour was passed through the monitors according to the invention at 3 litres/minute.

All monitors showed sensitivities to HTO better than 0.1 DAC . If inlet air containing plain water vapour was substituted by air containing tritiated water vapour, 50% of the final value was reached in less than 1 minute. The time response results were roughly what one would expect on the basis of complete mixing between the HTO in the passing air with the water in the zinc chloride solution. This conclusion was confirmed by tests which showed that the response time was inversely proportional to the flow rate.

Tests were subsequently conducted with various loadings of zinc chloride solution and with various relative humidities in the test gas. The effect of changing relative humidity, for a given HTO activity in the test gas, depended on the detector geometry and the amount of zinc chloride applied. Tests using a thickness of zinc chloride about 0.4 microns (at 60% r.h.) showed the least change in sensitivity with relative humidity.

There was a slight tendency for the monitors using plastic scintillator to reduce in sensitivity with time: this was ascribed to the redistribution of the deliquescent salt layer so as to make it less uniform in thickness. The effect was reduced by replacing the zinc sulphate solution by a polymeric gel of zinc sulphate solution.

CLAIMS:

1. A hygroscopic scintillator element suitable for selective response to tritiated water vapour and other hydrophilic tritiated species in a gas, which scintillator comprises a solid scintillator material having a layer of hygroscopic material thereon.

2. A scintillator element according to claim 1 wherein said solid scintillator material comprises any of, a plastic, an inorganic "phosphor" (such as doped zinc sulphide) an oxide based material, a glass or a combination of these materials.

3. A scintillator element according to claim 1 or 2 wherein said hygroscopic material comprises a layer of a hygroscopic or deliquescent substance as a solution or as an aqueous gel.

4. A scintillator element according to any preceding claim wherein said hygroscopic material comprises an aqueous or gel solution of a deliquescent salt, base or organic salt or an inorganic or organic substance which can absorb water, or a combination of any of said substances.

5. A scintillator element according to any preceding claim wherein said hygroscopic material is any of zinc chloride, potassium acetate, phosphoric acid or lithium chloride.

6. A scintillator element according to any preceding claim which further comprises a hydrated solid such as zeolite.

7. A scintillator element according to any preceding claim which is in the form of a sheet,

fibre, rod, spiral roll, powder, a powder compact, varnish, paint or a combination thereof.

8. A method for making a hygroscopic scintillator element, suitable for selective response to tritiated water vapour or other hydrophilic tritiated species in a gas, which method comprises coating a solid scintillator material with a layer of a hygroscopic material.

9. A method according to claim 8 which further comprises pre-treating the solid scintillator material with a detergent or subjecting it to a hydrophilic surface treatment.

10. A method according to claim 9 wherein said pre-treating step comprises sulfonation.

11. A method for monitoring the activity of tritiated water vapour or other hydrophilic tritiated species in a gas, which method comprises:

(a) providing a hygroscopic scintillator element according to any of claims 1 to 7 for contact with a gas to be tested;

(b) measuring the light emitted from said hygroscopic scintillator using measuring means, the amount of said light emitted from said scintillator element providing a measure of the activity of the tritiated water vapour or said hydrophilic tritiated species in the gas.

12. A method according to claim 11 wherein said hygroscopic scintillator is provided in an aperture in the wall of a substantially light-tight plant containing said gas, a suitable window or aperture being provided to allow said measuring means to measure only light emitted from the said hygroscopic

scintillator element.

13. A method according to claim 11 wherein said hygroscopic scintillator element is provided in a substantially light-tight container, which incorporates an inlet adapted to allow the access of said gas to said element and which prevents light entry to or escape from said container.

14. A method according to claim 11 which container additionally includes an outlet to allow passage of said gas therethrough.

15. A method according to any one of claims 9 to 14 wherein the light emitted by said hygroscopic scintillator is measured remotely by said measuring means spatially separated from said hygroscopic scintillator, but optically connected thereto.

16. A method according to any of claims 11 to 15 wherein the time averaged output of the measuring means is measured as a continuous current, and used to indicate the tritium radiotoxicity of said gas, and/or its tritiated water activity on a meter, a digital display as an audible signal, and/or as an output to a computer, data logger, recorder, control system.

17. A method according to any one of claims 9 to 16 wherein said measuring means comprises one or more photomultiplier tubes, multichannel plates or photodiodes.

18. A method according to claim 17 wherein the rate of signal pulses from said measuring means is measured and used to indicate the tritium radiotoxicity of said gas, and/or its tritiated water activity, on a meter, a digital display as an audible

signal, and/or as an output to a computer, data logger, recorder, or control system or the like.

19. A method according to claim 17 or 18 wherein more than one photomultiplier tube, multichannel plate or photodiode is provided.

20. A method according to any of claims 11 to 19 which further comprises using a non-discriminating tritium monitor in order to measure, by difference, the activities in said gas of both tritiated water and elemental tritium.

21. A method according to claim 20, wherein the non-discriminating monitor is substantially identical to the scintillator element according to any of claims 1 to 7, with the exception that the hygroscopic layer is omitted in the non-discriminating monitor.

22. A method according to any of claims 9 to 21 wherein said gas to be measured is air.

23. Apparatus for monitoring the activity of tritiated water vapour and other hydrophilic tritiated species in a gas, which apparatus comprises:

(a) a hygroscopic scintillator element according to any of claims 1 to 7; and

(b) means for measuring light emitted from said hygroscopic scintillator element, the amount of light emitted from said scintillator element providing a measure of the tritium containing species in said gas.

24. Apparatus according to claim 23 wherein said scintillator element is provided in a substantially light tight container including inlet means adapted to allow the gas to contact the scintillator element

without permitting entry or exit of light to or from said container.

25. Apparatus according to claim 23 or 24 which further comprises means for contacting said gas with said hygroscopic scintillator element.

26. Apparatus according to any of claims 23 to 25 which further comprises an outlet in said container to allow passage of said gas or vapour therethrough.

27. Apparatus according to claim 25 or 26 which comprises a pump to facilitate the passage of gas through said container.

28. Apparatus according to any of claims 23 to 27 wherein the light emitted by said hygroscopic scintillator element is measured remotely by said light measuring means spatially separated from said hygroscopic scintillator, but optically connected thereto by means of a light guide.

29. Apparatus according to any of claims 23 to 28 wherein said scintillator element is provided in the form of a sheet, fibre, rod, spiral roll, powder, a powder compact, varnish, paint, or a combination of said forms.

30. Apparatus according to any of claims 23 to 29 wherein said measuring means comprises one or more photomultiplier tubes, multichannel plates or photodiodes.

31. Apparatus according to claim 30 wherein the rate of signal pulses from said measuring means is measured and used to indicate the tritium radiotoxicity of said gas, and/or its tritiated water

activity, on a meter, a digital display, as an audible signal and/or as an electrical output to a computer, data logger, recorder or control electronics.

32. Apparatus according to claim 30 wherein a plurality of a photomultiplier tube, multichannel plate or photodiode is provided.

33. Apparatus according to claims 31 or 32 wherein the time averaged output of said measuring means is measured as a continuous current, and used to indicate the tritium radiotoxicity of said gas on a meter, a digital display as an audio signal, and/or as an output to a computer, data logger, recorder, control system or the like.

34. Apparatus according to any of claims 23 to 33 which further comprises a non-discriminating tritium monitor so as to measure, by difference, the concentrations in said gas or vapour of both tritiated water or other possible hydrophilic species and elemental tritium or other hydrophobic radioactive species present.

35. Apparatus, according to claim 34, wherein said non-discriminating monitor is substantially identical to a scintillator element according to any of claims 1 to 7, with the exception that the hygroscopic layer is omitted in the non-discriminating monitor.

36. Apparatus according to any of claims 23 to 35 which further comprises a second sealed radiation monitor to compensate for background radiation fields, by subtraction.

37. Apparatus according to claim 35 wherein said

sealed radiation monitor is substantially identical to the scintillator according to any of claims 1 to 5 and sealed in a container free of radioactive gas.

38. Apparatus according to claim 23 wherein the gas to be monitored comprises air.

39. Apparatus according to claim 23 which is incorporated in a breathing mask.

FIG. 1.

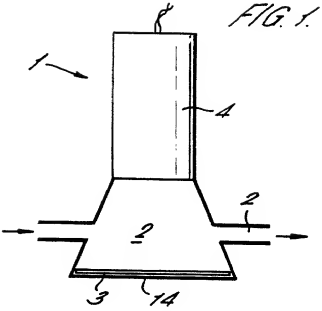


FIG. 2.

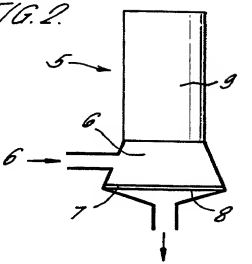


FIG. 3.

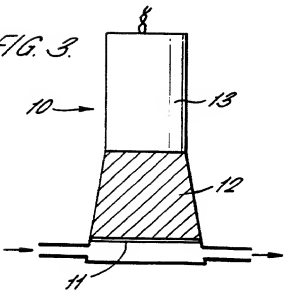


FIG. 4.

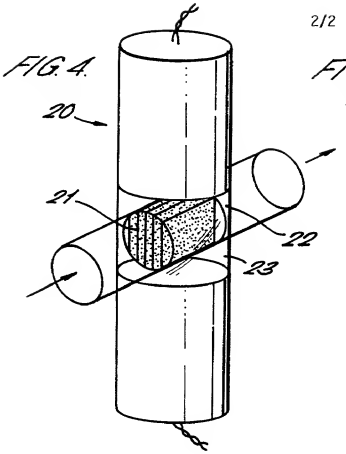


FIG. 5.

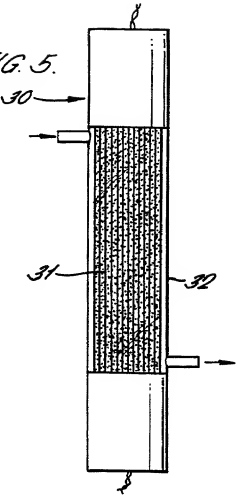


FIG. 6.

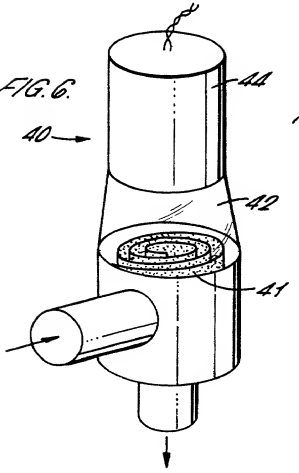
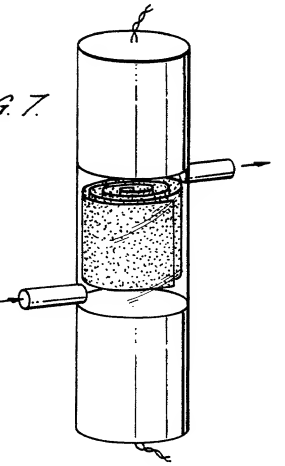


FIG. 7.



ATTORNEY/DOCKET NO. [illegible]

DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name; I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention (Design, if applicable) entitled:

SELECTIVE MONITORING OF TRITIUM-CONTAINING SPECIES IN A GAS

the specification of which was filed on: 22 September 1998 as International Application (PCT) No.:PCT/EP98/06047

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in *Title 37, Code of Federal Regulations, §1.56.* I hereby claim foreign priority benefits under *Title 35, United States Code §119* of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)			PRIORITY CLAIMED	
Number	*Country*	*Day/Month/Year Filed*	*Yes*	*No*
9720371.5	United Kingdom	24 September 1997	X	

I hereby claim the benefit under *Title 35, United States Code, §120* of any United States application(s) or PCT international application(s) designating The United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of *Title 35, United States Code, §112,* I acknowledge the duty to disclose information which is material to patentability as defined in *Title 37, Code of Federal Regulations, §1.56* which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

Application Number	*Filing Date*	*Status - Patented, Pending or Abandoned*

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under *section 1001 of title 18 of the United States Code* and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: I (We) hereby appoint as my (our) attorneys, with full powers of substitution and revocation, to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: J. Ernest Kenney, Reg. No. 19,179; Eugene Mar, Reg. No. 25,893; Richard E. Fichter, Reg. No. 26,382; Charles R. Wolfe, Jr., Reg. No. 28,680; Thomas J. Moore, Reg. No. 28,974; Bruce H. Troxell, Reg. No. 26,592; and

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DATE 8 March 2000	*SIGNATURE* RAH Edwards

See next page for additional inventors:

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PRIOR FOREIGN APPLICATION(S)			PRIORITY CLAIMED	
Number	*Country*	*Day/Month/Year Filed*	*Yes*	*No*
9720371.5	United Kingdom	24 September 1997	X	

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DATE 17. 3. 2000	*SIGNATURE*

See next page for additional inventors!